European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 92 20 2331

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,D, A	EP-A-0 443 686 (SHELL) * the whole document * ---	1-10	C07C2/34
D,A	EP-A-0 277 003 (EXXON) * claims; examples 23-24 * -----	1-10	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C07C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10 NOVEMBER 1992	ZERVAS B.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

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EPO FORM 1503 03.82 (P0401)

2. A process according to claim 1, characterised in that the further alpha olefin is a linear olefin having an odd number of carbon atoms.

3. A process according to claim 2, characterised in that the further alpha olefin is propene.

4. A process according to claim 1, characterised in that the further alpha olefin is styrene.

5. A process according to any of claims 1 to 4, characterised in that the ratio of the further alpha olefin(s) to ethene is within the range of from 50 to 500 moles per mole ethene.

6. A process according to any of claims 1 to 5, characterised in that the oligomerisation is carried out at a temperature within the range of from 50 to 150 °C and at a pressure within the range of from 5 to 60 bar.

7. A process according to any of claims 1 to 6, characterised in that the molar ratio of the first component to the second component of the catalyst system is within the range of from 0.1 to 5.0.

8. A process according to any of claims 1 to 8, characterised in that such a quantity of the catalyst system is employed in the reaction mixture as to contain from 10^{-3} to 10^{-5} gram atom of the Group IVA metal per mole of ethylene to be reacted.

9. A process according to any of claims 1 to 8, characterised in that the first component of the catalyst system is a compound of formula $(Cp)_2MR_1R_2$ where each group Cp, which may be the same or different, represents a cyclopentadienyl group of which at least one is (cyclo)alkyl and/or arylalkyl substituted, M represents a group IVA metal atom, and R_1 and R_2, which may be the same or different, each represent a hydrogen atom or a substituted or unsubstituted hydrocarbyl group, and in that the second component of the catalyst system is a trialkylammonium carborane, the carborane anion being represented by the formula $B_{11}CH_{12}^{-}$.

10. A process according to claim 9, characterised in that M is zirconium or hafnium, and each group Cp represents a pentamethylcyclopentadienyl group and R_1 and R_2 are each alkyl groups.

Table 4

Example in EP-91200367.0	Catalyst 1)	Ethylene g	Molar ratio 2)
1	C	8.4	0.3
2	C	11.8	0.4
3	D	11.8	0.4
4	C	25	0.4
5	C	2.3	4.3
6 3)	C	19.3	0.3
8	E	17.8	0.14

1) C: contained bis(cyclopentadienyl)zirconium dimethyl
D: contained bis(pentamethylcyclopentadienyl)zirconium dimethyl
E: contained bis(pentamethylcyclopentadienyl)hafnium dimethyl

2) of further alpha olefin to ethene

3) Identical to Comparative Example 1 described hereinbefore

The data of Table 4 shows that the reaction conditions of the Examples of EP-91200367.O are outside the scope of the process of the invention.

In Examples 6 and 7, styrene was used as the further alpha olefin with ethene. Comparison of the results shows that in Example 7, which is according to the invention, relatively more of the co-oligomers is formed, and relatively more of the alpha-oligomers and alpha-co-oligomers, than in comparative Example 6.

Claims

1. A process for the preparation of olefins of the general formula $R\text{-}(CH_2\text{-}CH_2)_p\text{-}CH=CH_2$ in which formula R is a hydrocarbyl group and p is an integer of at least 1, comprising reacting ethene with at least one further alpha olefin of the general formula $R\text{-}CH=CH_2$ under oligomerisation conditions in the presence of a catalyst system obtainable by combining a first component which is a bis(cyclopentadienyl) Group IVA metal compound containing a substituent which is attached to the metal and which is capable of reacting with a cation, and a second component which is a compound having a bulky anion containing a plurality of boron atoms and which is substantially non-coordinating under the reaction conditions and a cation, and recovering an oligomeric product comprising linear olefins of the general formula $R\text{-}(CH_2\text{-}CH_2)_p\text{-}CH=CH_2$, wherein the further alpha olefin(s) and ethene are present in a molar ratio of at least 1 and wherein at least one of the cyclopentadienyl groups of the metal compound is (cyclo)alkyl and/or arylalkyl substituted.

Table 3 (continued)

Example	$6^{1)}$		7	
Distribution of ethene/styrene co-oligomers (g)	α	β	α	β
$C_{10}^{=}$	0.16	0.13	0.40	0.04
$C_{12}^{=}$	0.17	0.17	0.47	0.08
$C_{14}^{=}$	0.09	0.11	0.40	0.07
$C_{16}^{=}$	0.05	0.06	0.34	0.06
$C_{18}^{=}$	0.03	0.03	0.28	0.05
$C_{20}^{=}$	0.02	0.03	0.24	0.05
$C_{22}^{=}$	0.01	0.01	0.20	0.03
$C_{24}^{=}$	0.01	0.01	0.17	0.02
$C_{10}^{=} - C_{24}^{=}$	0.54	0.55	2.50	0.40
Total $C_{10}^{=} - C_{24}^{=}$, α + β	0.99		2.90	
Ratios, on weight basis				
α/β, oligomers	0.71		6.79	
α/β, co-oligomers	0.98		6.25	
Total co-oligomers/oligomers	0.22		0.72	

1) For comparison

Examples 2, 4, 5 and 7 are according to the invention. In these Examples the molar ratio of the further alpha olefin to ethene is more than 1 and the cyclopentadienyl is alkyl substituted. Examples 1, 3 and 6 are not according to the invention. They have been included as comparative examples. In Examples 1, 3 and 6 the cyclopentadienyl group was unsubstituted. In Examples 1 and 6 the molar ratio of the further alpha olefin to ethene is less than 1, whilst in Example 3 this ratio is more than 1.

By comparison of Examples 2 - 5 with Example 1 it can be seen that increase of the molar ratio of propene over ethene leads to a substantial increase of the selectivity S, which implies a substantial increase of the formation of co-oligomers of propene and ethene over the formation of oligomers of ethene. Comparison of Example 3 with Example 1 shows that the increase of the molar ratio of the olefins does not influence the relative quantities of the alpha olefins among the co-oligomerisation products. Relatively high proportions of alpha olefins among the co-oligomerization products are achieved by using a bis-(cyclopentadienyl) metal compound derived from an alkyl substituted cyclopentadienyl (cf. Example 2 vs. Example 1 and Examples 4 and 5 vs. Example 3). Examples 2, 4 and 5 show, in addition, that a relatively high proportion of the branched olefins which are formed in the co-oligomerisation of propene and ethene are iso-alkenes having an even number of carbon atoms.

Comparative Example 1 of the present application is a reproduction of Example 6 of the Applicant's earlier dated European patent application 91200367.0, mentioned hereinbefore, supplemented with additional data. The amount of ethene initially present in the reaction mixtures of the Examples of EP-91200367.0 and the corresponding molar ratios of the further olefin to ethene are given in Table 4.

Table 3

Example		6[1])		7	
Catalyst liquor		A		B	
Styrene charge (g)		19.8		19.8	
Ethene initial charge (g)		8.5		3.1	
Molar ratio styrene/ethene		0.63		1.73	
Reaction temperature (°C)		90		125	
Pressure (bar)		10		5	
Reaction time (min)		30		30	
Olefin yields (g) C_4^{-} - $C\bar{3}6$		9.0		10.6	
Distribution of ethene oligomers (g)		α	β	α	β
	$C\bar{6}$	0.73	1.23	0.58	0.09
	$C\bar{8}$	0.47	0.57	0.57	0.08
	$C\bar{1}0$	0.27	0.33	0.52	0.07
	$C\bar{1}2$	0.16	0.20	0.47	0.07
	$C\bar{1}4$	0.10	0.11	0.42	0.06
	$C\bar{1}6$	0.06	0.07	0.37	0.06
	$C\bar{1}8$	0.03	0.04	0.32	0.05
	$C\bar{2}0$	0.02	0.03	0.28	0.04
	$C\bar{6}$ - $C\bar{2}0$	1.84	2.58	3.53	0.52
Total	$C\bar{6}$ -$C\bar{2}0$, α + β	4.48		4.05	

Table 2 (continued)

Example	3 [1]	4	5
octenes (g)	0.07	0.03	0.05
1-octene (%w)	54.0	50.0	80
2-octenes (%w)	36.0	6.7	10
iso-octenes (%w)	10	43.3	10
nonenes (g)	0.05	0.26	0.64
1-nonene (%w)	48.0	76.8	48.0
2-nonenes (%w)	32.0	6.6	6.9
iso-nonenes (%w)	20	16.6	45.1
Selectivity S (%)	61	72	71

1) for comparison
2) bis(cyclopentadienyl)zirconium dimethyl
3) bis(pentamethylcyclopentadienyl)zirconium dimethyl
4) bis(pentamethylcyclopentadienyl)hafnium dimethyl

Examples 6 and 7

The procedures were carried out with rigorous exclusion of oxygen and moisture.

In comparative Example 6, catalyst liquor A as described in Example 1 (1 mmol of both ingredients) was applied.

In Example 7, catalyst liquor B as described in Example 2 (1 mmol of both ingredients) was applied.

The oligomerisation reaction was performed as in Examples 1 and 2, the reactants being styrene and ethene. The product distribution was determined by GLC on a sample taken from the content of the autoclave after terminating the reaction.

Details of the reaction conditions and of the analytical results are given in Table 3.

Table 2

Example	3 1)	4	5
Metal compound (mmol)	1.0 2)	0.05 3)	0.05 4)
$Bu_3NHB_{11}CH_{12}$ (mmol)	1.0	0.05	0.05
Propene charge (g)	300	100	100
Ethene initial charge (g)	3.0	0.5	0.5
Molar ratio $C_3^=/C_2^=$	67	133	133
Total volume of toluene (ml)	300	100	100
Reaction temperature (°C)	125	150	150
Pressure (bar)	30	50	50
Reaction time (min)	60	16	8
Olefin yields, GLC (g)			
C_4 - C_9 olefins	3.37	5.83	16.29
C_{10}^+ olefins	0.17	0.35	2.42
Distribution C_4 - C_9 olefins			
butene (g)	0.43	0.36	1.20
1-butene (%w)	58.0	95.8	97.5
2-butenes (%w)	42.0	4.2	2.5
pentenes (g)	1.70	3.01	8.95
1-pentene (%w)	47.3	91.2	86.9
2-pentenes (%w)	23.7	6.3	12.1
2-methyl-1-butene (%w)	29.0	2.5	1.0
hexenes (g)	0.81	1.21	3.36
1-hexene (%w)	11.5	8.5	2.4
2-hexenes (%w)	8.5	0.8	0.6
2-methyl-1-pentene (%w)	78.0	68.0	53.0
4-methyl-1-pentene (%w)	2.0	22.7	44.0
heptenes (g)	0.31	0.96	2.09
1-heptene (%w)	39.4	79.5	81.1
2-heptenes (%w)	28.6	6.9	11.7
iso-heptene (%w)	32.0	13.7	7.1

Examples 3, 4 and 5

The procedures were carried out with rigorous exclusion of oxygen and moisture.

An autoclave (500 ml volume) was charged with toluene, ethene, propene and tri-n-butylammonium 1-carbadodecacarborate of formula $Bu_3NHB_{11}CH_{12}$. After heating the contents of the autoclave to the reaction temperature, a solution of one of the following metal compounds in about 10 ml toluene was introduced into the autoclave. In comparative Example 3 bis(cyclopentadienyl)zirconium dimethyl was used as the metal compound, in Example 4 bis(pentamethylcyclopentadienyl)zirconium dimethyl and in Example 5 bis-(pentamethylcyclopentadienyl)hafnium dimethyl. After introduction of the metal compound, ethene was continuously supplied to the autoclave at a rate of about 0.3 g/min in Example 3 and at a rate of about 1 g/min in Example 5, whilst in Example 4 the pressure in the autoclave was maintained by continuously recharging of consumed ethene. The reaction was terminated by releasing the pressure in the autoclave, exposing the contents to air and adding methanol. The product distribution was determined by analyzing a sample taken from the content of the autoclave gas-liquid chromatography (GLC). The selectivity is assessed by calculating the selectivity S as defined for Examples 1 and 2.

Details of the reaction conditions and of the analytical results are given in Table 2.

Table 1 (continued)

Example	1 [1])	2	
Olefin yields, GLC (g)			
C_4 - C_9 olefins	21.36	14.82	22.06
C_{10}^{+} olefins	11.39	-	37.94
Distribution C_4 - C_9 olefins			
butene (g)	7.02	0.82	1.78
1-butene (%w)	47.8	86.6	83.7
2-butenes (%w)	52.2	13.4	16.3
pentenes (g)	1.42	4.99	4.90
1-pentene (%w)	50.1	84.0	73.9
2-pentenes (%w)	35.9	15.5	25.5
2-methyl-1-butene (%w)	14.0	0.6	0.6
hexenes (g)	6.49	1.01	2.75
1-hexene (%w)	58.5	54.5	75.3
2-hexenes (%w)	38.9	8.9	10.6
2-methyl-1-pentene (%w)	2.6	36.6	14.2
4-methyl-1-pentene (%w)	0.0	0.0	0.0
heptenes (g)	0.87	3.97	5.24
1-heptene (%w)	59.4	83.4	76.2
2-heptenes (%w)	29.8	15.4	22.9
iso-heptene (%w)	10.8	1.3	1.0
octenes (g)	4.85	0.97	2.72
1-octene (%w)	66.1	50.5	75.4
2-octenes (%w)	30.1	8.3	9.9
iso-octenes (%w)	3.8	41.2	14.7
nonenes (g)	0.71	3.06	4.83
1-nonene (%w)	58.8	83.3	78.1
2-nonenes (%w)	29.4	15.4	21.1
iso-nonenes (%w)	11.8	1.3	0.8
Selectivity S (%)	12	79	65

[1]) for comparison

[2]) A contained bis(cyclopentadienyl)zirconium dimethyl
B contained bis(pentamethylcyclopentadienyl)zirconium dimethyl

$$S = \frac{\text{yield of } C_5^{=} + C_7^{=} + C_9^{=} \text{ (moles)}}{\text{yield of } C_4^{=} + C_5^{=} + C_6^{=} + C_7^{=} + C_8^{=} + C_9^{=} \text{ (moles)}}$$

Details of the reaction conditions and of the analytical results are given in Table 1.

Table 1

Example	1 [1)]	2	
Catalyst liquor [2)]	A	B	
Propene charge (g)	10	23	
Ethene initial charge (g)	19.3	7	
Molar ratio $C_3^{=}/C_2^{=}$	0.35	2.2	
Reaction temperature (°C)	125	90	
Pressure (bar)	30	15	
Reaction time (min)	30	2	15

groups are pentamethylcyclopentadienyl groups. R_1 and R_2 are preferably alkyl groups, typically of up to 5 carbon atoms, such as methyl.

Such complexes are known and can be prepared for example by the routes described in "Chemistry of Organo-Zirconium and Hafnium Compounds", by Lappert et al., published by John Wiley & Sons.

The second component preferably contains, as the boron containing substantially non-coordinating anion, a carborane anion, suitably a carborane anion of formula $B_{11}CH_{12}^{-}$, while the cation is preferably a proton donating cation, preferably a quaternary ammonium cation such as a trialkylammonium cation, for example tri-n-butylammonium cation. Alternatively the cation may be a metal cation, such as a silver ion. Such carboranes are known and can be prepared for example by methods such as that of Shelly et al, J. Am. Chem. Soc., 1985, Vol. 107, p. 5955 to 5959. Other bulky boron containing anions may be used such as a tetra(perfluorophenyl)boron anion.

The catalyst system may be formed by mixing together the two components, preferably in solution in a solvent such as toluene to form a liquid catalyst system. The two compounds are generally employed in substantially equimolar amounts. However the molar ratio of the first compound to the second compound may vary within the range of from 0.1 to 5.0. Such a quantity of the catalyst system is usually employed in the reaction mixture as to contain from 10^{-1} to 10^{-7} gram atom, in particular 10^{-3} to 10^{-5} gram atom, of the Group IVA metal per mole of ethylene to be reacted.

The oligomerisation is generally, although not necessarily, carried out in an inert liquid solvent which is suitably also the solvent for the catalyst components. The reaction can be carried out in batch or continuous operation. Reaction times of from 1 minute to 5 hours have been found to be suitable, dependent on the activity of the catalyst. After a suitable reaction time, a conventional catalyst deactivating agent such as methanol, or another alcohol, may be added if desired to the reaction mixture to terminate the reaction. The resulting mixed olefins preferably have a chain length of from 5 to 24 carbon atoms. The reaction is preferably carried out in the absence of air or moisture.

Product olefins are recovered suitably by distillation and further separated as desired by distillation techniques dependent on the intended end use of the olefins. If desired, unconverted starting material and oligomeric product having a molecular weight which is lower than the desired molecular weight may be recovered and recycled to be used as starting material in a subsequent oligomerisation reaction.

The invention will now be illustrated by the following examples.

Examples 1 and 2

The procedures were carried out with rigorous exclusion of oxygen and moisture.

Catalyst liquors were prepared by combining the following ingredients.

Catalyst liquor A, applied in comparative Example 1:

bis(cyclopentadienyl)zirconium dimethyl (0.251 g, 1.00 mmol). tri-n-butylammonium 1-carbadodecacarborate of formula $Bu_3NHB_{11}CH_{12}$ (0.329 g, 1.00 mmol, Bu = n-butyl), toluene (30 ml)

Catalyst liquor B, applied in Example 2:

bis(pentamethylcyclopentadienyl)zirconium dimethyl (0.196 g, 0.50 mmol) $Bu_3NHB_{11}CH_{12}$ (0.164 g, 0.50 mmol) toluene (30 ml)

The catalyst liquors were added to an autoclave (500 ml volume) containing propene together with toluene (270 ml in Example 1, 70 ml in Example 2). The autoclave was then pressurised with ethene, using a predetermined quantity of ethene, and rapidly heated to the reaction temperature. Pressure was maintained by continuously recharging of consumed ethene. The reaction was terminated by releasing the pressure in the autoclave, exposing the contents to air and adding methanol. The product distribution was determined by analysing a sample taken from the content of the autoclave with gas-liquid chromatography (GLC).

In order to assess the selectivity of the co-oligomerisation relative to ethene oligomerisation a selectivity S is calculated which is defined by:

The starting reactants comprise ethene, which may be supplied in the form of an ethene-containing gas together with an inert diluent such as nitrogen or helium. The further alpha olefins are suitably alpha olefins containing from 3 to 20 carbon atoms, such as 1-butene, 4-methyl-1-pentene, 5,5-dimethyl-1-hexene, styrene or allylbenzene, dependent on the desired oligomerisation product. Mixtures of alpha olefins may be employed.

When the fur-her alpha olefin is linear and has an odd number of carbon atoms, the oligomeric products $R\text{-}(CH_2\text{-}CH_2)_p\text{-}CH=CH_2$ comprise olefins having odd numbers of carbon atoms. It has been found in performing the process according to the invention that when oligomeric branched olefins are formed as by-products, these branched olefins are to a large extent iso-alkenes of the general formula $R\text{-}(CH_2\text{-}CH_2)_p\text{-}CH=CH_2$, in which formula R and p have the meanings given hereinbefore, especially when the oligomerisation is carried out at a temperature below 120 °C, in particular below 100 °C. As the further olefin has an odd number of carbon atoms, these iso-alkenes have even numbers of carbon atoms. As a consequence, the desired linear oligomerisation products differ from the iso-alkenes by at least one carbon atom and can therefore relatively easily be recovered by separation from the iso-alkenes, for example by distillation. Thus, in the case that the further alpha olefin is linear and has an odd number of carbon atoms it is an unexpected advantage of the present process that the linear oligomerisation products can relatively easily be obtained in a purified state. Accordingly, the preferred further alpha olefin is linear and has an odd number of carbon atoms, in particular of less than 20, for example, propene, 1-pentene and 1-heptene or mixtures thereof. The most preferred further alpha olefin is propene.

When the further alpha olefin is an aryl substituted alpha olefin, such as in particular styrene, it has been found in performing the process according to the invention that a relatively large proportion of the product oligomers formed are the co-oligomers (as distinct from the ethene oligomers).

In both cases, when the further alpha olefin is linear and when it is aryl substituted, it has been found in performing the process according to the invention that a relatively large proportion of the product olefins are alpha olefins.

The relative proportions of starting monomers present in the reaction mixture should be at least I mole of the further alpha olefin(s) per mole of ethene. Suitably the quantity of the further alpha olefin(s) is at least 20 moles per mole of ethene, more suitably at least 50 moles per mole of ethene. Preferably the quantity of the further alpha olefin(s) is less than 1000 moles per mole of ethene, more preferably less than 500 moles per mole of ethene. Ethene and the further olefin(s) may be supplied at the initial stage of the co-oligomerisation. In a preferred embodiment of the present process, the ethene to be reacted is only partly supplied at the initial stage of the reaction, the remainder of the ethene being supplied in the course of the reaction, typically at a rate which is suitable to replenish the ethene consumed.

To effect oligomerisation, the reaction is suitably carried out at elevated temperatures, preferably in the range of from 20 to 175 °C, more preferably 50 to 150 °C. The reaction is suitably carried out under conditions of moderate elevated pressure, preferably in the range of from 1 to 100 bar, more preferably from 5 to 60 bar. The optimum conditions of temperature and pressure used for a particular catalyst system to maximise the yield of the desired oligomer and minimize competing reactions such polymerisation can readily be established by those skilled in the arc.

The catalyst system, which may be formed initially prior to introduction to the reaction vessel, or which may be formed in situ, may be obtainable by combining a first component which is a bis(cyclopentadienyl) Group IVA metal compound having a substituent which is attached to the metal and which is capable of reacting with a proton and at least one of the cyclopentadienyl groups being (cyclo)alkyl and/or arylalkyl substituted, and a second component which is an ionic combination of a bulky anion containing a plurality of boron atoms and a proton-donating cation, the anion being such that it is substantially non-coordinating under the reaction conditions employed. Thus, it is intended that the anion should not coordinate, or at least coordinate only weakly, to the bis(cyclopentadienyl) metal entity which is formed by reaction of the donated proton and the acceptor substituent of the first compound. Examples of such catalyst systems, normally regarded as polymerisation catalysts (as distinct from oligomerisation catalysts), are to be found in EP-A-277003 and in the paper by Hlatky et al, J. Am. Chem. Soc., 1989, Vol. 111 p. 2728-2729.

The first component is typically a compound of zirconium or hafnium. The compound preferably has the formula $(Cp)_2MR_1R_2$ where each group Cp, which may be the same or different, represents a cyclopentadienyl group of which at least one is (cyclo)alkyl and/or arylalkyl substituted, M represents a Group IVA metal atom, typically zirconium or hafnium, and R_1 and R_2 which may be the same or different, each represent a hydrogen atom or a substituted or unsubstituted hydrocarbyl group. Preferably the groups Cp are the same and have in particular at least three substituents, more in particular five substituents. The substituent(s) of the cyclopentadienyl are typically alkyl groups, in particular having up to 5 carbon atoms, more in particular they are methyl groups. Very good results can be achieved when both cyclopentadienyl

This invention relates to a co-oligomerisation process and is particularly directed to the preparation of olefins of the general formula R-$(CH_2-CH_2)_p$-CH = CH_2 in which formula R is a hydrocarbyl group and p is an integer of at least 1, comprising reacting ethene with at least one further alpha olefin of the general formula R-CH = CH_2.

Oligomerisation processes for the production of linear alpha olefins are well known. For example, from GB-A-1353873 it is known that C_6-C_{20} linear alpha olefins can be prepared from ethene by oligomerisation in the presence of a nickel containing catalyst. Linear olefins, especially linear alpha olefins, over a range of carbon chain lengths have found use as valuable intermediates in the preparation of polyolefins, detergents and lubricant additives. While the known processes for the oligomerisation of ethene provide linear olefins of which the number of carbon atoms is even, for certain application areas of olefins it is desirable to have at one's disposal olefins which have special structural features, such as linear alpha olefins which have an odd number of carbon atoms or alpha olefins which have one or more hydrocarbyl substituents located at or near the end of the carbon chain opposite to the end at which the double bond is located. The object of the present invention is the provision of an oligomerisation process by which olefins having such special structural features can conveniently be prepared.

A process for the preparation of olefins of the general formula R-$(CH_2-CH_2)_p$-CH = CH_2 in which formula R is a hydrocarbyl group and p is an integer of at least 1, comprising reacting ethene with at least one further alpha olefin of the general formula R-CH = CH_2 under oligomerisation conditions in the presence of a catalyst system obtainable by combining a first component which is a bis(cyclopentadienyl) Group IVA metal compound containing a substituent which is attached to the metal and which is capable of reacting with a cation, and a second component which is a compound having a bulky anion containing a plurality of boron atoms and which is substantially non-coordinating under the reaction conditions and a cation, and recovering an oligomeric product comprising linear olefins of the general formula R-$(CH_2-CH_2)_p$-CH = CH_2, is the subject matter of the Applicant's non-prepublished European patent application 91200367.0 of earlier date. By this co-oligomerisation process it is possible to prepare mixtures comprising co-oligomers of high linearity which may have an odd or an even number of carbon atoms and which have a high content of alpha olefins. These oligomeric products are prepared in conjunction with oligomers of ethene, from which they have to be separated to obtain them in a state of high purity. This separation may in some instances be difficult to perform.

It has now been found that, when in this process the further alpha olefin, designated by the general formula R-CH = CH_2, in which R is defined as hereinbefore, is present in the reaction mixture in a quantity of at least 1 mole per mole of ethene and at least one of the cyclopentadienyls of the Group IVA metal compound is (cyclo)alkyl and/or arylalkyl substituted, an oligomerisation product can be obtained which has a high content of olefins of the general formula R-$(CH_2-CH_2)_p$-CH = CH_2, in which R and p have the meanings given hereinbefore. The oligomerisation product thus obtained has a relatively low content of other oligomers, for example oligomers of ethene and different co-oligomers of ethene and the further alpha olefin, such as co-oligomers which have the double bond in the 2-position.

Products of the general formula R-$(CH_2-CH_2)_p$-CH = CH_2 may comprise linear alpha olefins which have an odd number of carbon atoms or alpha olefins which have one or more hydrocarbyl substituents located at or near the end of the carbon chain opposite to the double bond. Therefore, the present process is capable of providing olefins with special structural features as indicated hereinbefore, in a single step from readily available feedstock. The desired oligomeric alpha-olefins can be prepared with relatively little-formation of by-products and, accordingly, they can be purified relatively easily. The present process therefore constitutes an improvement over the process described in the Applicant's earlier European patent application 91200367.0.

Accordingly, the present invention provides a process for the preparation of olefins of the general formula R-$(CH_2-CH_2)_p$-CH = CH_2 in which formula A is a hydrocarbyl group and p is an integer of at least 1, comprising reacting ethene with at least one further alpha olefin of the general formula R-CH = CH_2 under oligomerisation conditions in the presence of a catalyst system obtainable by combining a first component which is a bis(cyclopentadienyl) Group IVA metal compound containing a substituent which is attached to the metal and which is capable of reacting with a cation, and a second component which is a compound having a bulky anion containing a plurality of boron atoms and which is substantially non-coordinating under the reaction conditions and a cation, and recovering an oligomeric product comprising linear olefins of the general formula R-$(CH_2-CH_2)_p$-CH = CH_2, wherein the further alpha olefin(s) and ethene are present in a molar ratio of at least 1 and wherein at least one of the cyclopentadienyl groups of the metal compound is (cyclo)alkyl and/or arylalkyl substituted.

Metals of Group IVA are as defined in the Periodic Table of the Elements published in Kirk-Othmer, Encyclopaedia of Chemical Technology, 2nd edition, Vol. 8, p. 94.

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(54) Co-oligomerisation process.

(57) A process for the preparation of olefins of the general formula $R-(CH_2-CH_2)_p-CH=CH_2$ in which formula R is a hydrocarbyl group and p is an integer of at least 1, comprising reacting ethene with at least one further alpha olefin of the general formula $R-CH=CH_2$ under oligomerisation conditions in the presence of a catalyst system obtainable by combining a first component which is a bis(cyclopentadienyl) Group IVA metal compound containing a substituent which is attached to the metal and which is capable of reacting with a cation, and a second component which is a compound having a bulky anion containing a plurality of boron atoms and which is substantially non-coordinating under the reaction conditions and a cation, and recovering an oligomeric product comprising linear olefins of the general formula $R-(CH_2-CH_2)_p-CH=CH_2$, wherein the further alpha olefin(s) and ethene are present in a molar ratio of at least 1 and wherein at least one of the cyclopentadienyl groups of the metal compound is (cyclo)alkyl and/or arylalkyl substituted.

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